Inter- and Intramolecular Interactions of Polymer as Studied by Fluorescence Spectroscopy. XI. Solvent and Concentration Effects on the Exciplex Emission by Poly[oxy-2-(1-pyrenylmethyl)propyleneoxy-(4-*N,N*-dimethylaminobenzyl)malonyl]

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ABSTRACT: Solvent and concentration effects on the exciplex formation by poly[oxy-2-(1-pyrenylmethyl)propyleneoxy-(4-*N,N*-dimethylaminobenzyl)malonyl] (**I**) ($DP < 18$) are discussed for three solvents. The dimer model compound, 1-acetoxy-2-(1-pyrenylmethyl)propyleneoxy-(4-*N,N*-dimethylaminobenzyl) malonyloxyethane (**II**) was prepared from the corresponding halfester of the 1,3-propanediol with the corresponding diethyl malonate. From the results of absorption, emission and excitation spectra, the solvent and molecular weight effects on inter- and intramolecular interactions of the **I** system were compared with those of **II**. The ratio of exciplex emission intensity (F_e) to monomer emission intensity by pyrenyl groups (F_m) increased with concentration, suggesting an interpolymer association of **I** in a concentration region below 10^{-5} M whereas exciplex by **II** was concentration independent. When the initial slopes of F_e/F_m vs. concentration were plotted against the degree of polymerization (DP), there was found an optimum DP for intermolecular interactions of the polymer. The facts that the interpolymer exciplex formation was most efficient in the intermediate DP region, and that the optimum DP value for interpolymer association was higher in a good solvent (1,2-dichloroethane) than in a poor solvent (mesitylene), may be considered as important findings. The mixing of emission by an excited ground state complex with true exciplex emission was suggested by the dependence of the shape of the apparent exciplex emission on the excitation wavelength.

KEY WORDS Polyester / Exciplex / Molecular Association / Donor Acceptor Interaction / Fluorescence / Pyrene / *N,N*-Dimethylaniline / Solvent Effect / Zipping Effect /

Exciplex formation in polymeric systems is useful for investigating molecular interactions in both ground and excited states. In the past few years, we have investigated a variety of exciplex forming donor-acceptor pairs bound to polymers.¹⁻⁷ A comparison with small molecular model system shows that there are several distinct differences in polymer bound exciplexes. First of all, exciplex emission in polymeric systems is enhanced in part by interpolymer association in the ground state and in part by protecting the exciplex from solvation by the polymer chain. The self association phenomenon seems to be a common feature of exciplex forming polymers having well defined repeating

units, whereas excimer forming polymers do not self associate unless the polymer concentration is much higher than that of the exciplex forming polymers. Apparently, a study on exciplexes provides more information on microenvironments of polymers than that expected from an excimer study, since exciplex is sensitive to solvation and solvent polarity.

Recently, we reported that a polyester having pyrenyl and *N,N*-dimethylanilino groups in an alternative fashion emits strong exciplex emission and interpolymer association takes place even below 10^{-5} M. Furthermore, the interpolymer association proceeds allosterically.⁸ These phenomena were ex-

plained as due to a zipping interaction of a weak donor-acceptor pair in the ground state. If this is the case, the spectroscopic behavior of exciplex forming polymers should depend on the degree of polymerization and solvent, both of which are controlling factors of polymer chain dimension and entanglement.

The purpose of the present article is to present an explanation of the experimental details of the previous report⁸ and to demonstrate the molecular weight and solvent effects on interpolymer exciplex formation by the exciplex forming polyester **I**. In this particular study sample preparation has been a key step. Previous exciplex polymers were of low degree of polymerization. In particular, an analogous polyester having 9-anthryl and *N,N*-dimethylanilino groups could not be obtained as a high molecular weight sample presumably because of the steric effect of the diol monomer bearing an anthryl group.⁷ Polycondensation of 2-(1-pyrenylmethyl)-1,3-propanediol with diethyl (4-*N,N*-dimethylaminobenzyl) malonate proceeded more smoothly ($DP < 18$) than its corresponding anthryl analogue. In addition to the synthetic advantage, a pyrene-*N,N*-dimethylaniline pair is a better combination than an anthracene-*N,N*-dimethylaniline pair since the exciplex has a larger emission probability and the photophysical behavior has been best studied in small molecular systems.

EXPERIMENTAL

Materials

Preparation of the polyester (**I**) and the pyrene monomer model (**III**)¹² and the DMA monomer model (**IV**)⁶ has been already described. The dimer model compound (**II**) was synthesized in the following way.

1-Acetoxy-2-(1-pyrenylmethyl)-3-propanol (**V**). An equimolar amount of 2-(1-pyrenylmethyl)-1,3-propanediol was reacted with acetyl chloride in tetrahydrofuran after stirring for 8 h at room temperature, then was purified on a silica gel column. Yield 50.5% (oil); IR (KBr disk) 1734 cm^{-1} ($\nu_{\text{C=O}}$), 3400 cm^{-1} ($-\text{OH}$); NMR (CDCl_3) δ 2.05 (3H, s, $-\text{C}(=\text{O})\text{CH}_3$), δ 2.1–2.4 (1H, m, $>\text{CH}$), δ 3.30 (2H, d, $J=7.2\text{ Hz}$, $-\text{CH}_2\text{-Py}$), δ 3.60 (2H, d, $J=7.2\text{ Hz}$, $-\text{CH}_2\text{-O}-\overset{\text{O}}{\parallel}{\text{C}}-$), δ 4.20 (2H, d, $J=7.8\text{ Hz}$,

$-\text{CH}_2\text{OH}$), δ 7.8–8.2 (9H, m, $-\text{Py}$).

1-Acetoxy-2-(1-pyrenylmethyl) propyleneoxy (4-*N,N*-dimethylaminobenzyl)malonyloxyethane (**II**). An equimolar mixture of **V** and diethyl (4-*N,N*-dimethylaminobenzyl)malonate was reacted in bulk using calcium acetate as a catalyst. The reaction was conducted under a nitrogen atmosphere at normal pressure at 160°C for two hours. The product was dissolved in THF, and then was purified on a silica gel column. Yield 34% (oil); Analytical data; E.A. Calcd for $\text{C}_{36}\text{H}_{37}\text{O}_6\text{N}$: C, 74.59%, H, 6.43%; N, 2.42%. Found: C, 74.67%; H, 6.43%; N, 2.36%. NMR (CD_2Cl_2) δ 1.13 (3H, t, $J=7\text{ Hz}$, $-\text{CH}_2\text{CH}_3$), δ 2.05 (3H, s, $-\text{C}(=\text{O})\text{CH}_3$), δ 2.76 (6H, s, $-\text{N}(\text{CH}_3)_2$), δ 3.08 (2H, d, $J=8\text{ Hz}$, $-\text{CH}_2\text{-DMA}$), δ 3.16 (2H, m, $-\text{CH}_2\text{Py}$), δ 3.68 (1H, t, $J=9\text{ Hz}$, $>\text{CH}-\text{CH}_2\text{-DMA}$), δ 4.12 (6H, m, $-\text{CH}_2\text{-O}-$), δ 6.60–7.2 (4H, m, $-\text{Ar}$), δ 7.9–8.3 (9H, m, $-\text{Py}$). Molecular weight data for **II** Calcd; 579.7. Found; 584.0 by vapor pressure osmometry method.

Solvent

Mesitylene was washed in concentrated sulfuric acid, then dried and distilled. *p*-Dioxane was refluxed over sodium metal and distilled. Other solvents were purified by accepted procedures.

Spectroscopy

The absorption and fluorescence spectra were recorded by a Shimadzu UV-200 spectrometer and a Hitachi MPF-4 spectrofluorometer, respectively. The fluorescence spectroscopy was conducted under an argon atmosphere. For "true" excitation spectrum measurements, the concentration of samples was kept at $\text{O.D.}_{\text{max}} < 0.05$ (O.D._{max} : the maximum optical density of the sample solution) and the spectra were corrected for the instrumental factors. The molarity of the polymer solution was based on the "repeating unit" concentration.

RESULTS

Absorption Spectra

Absorption spectra of polymer (**I**) and the corresponding model compound (**II**) and monomer models (**III** and **IV**) are shown in Figure 1. The S_0-S_2 absorption band of **II** agreed with 1,3-bisacetoxy-2-(1-pyrenylmethyl)propane (**III**) whereas that of **I** showed a red shift by 2–3 nm.

Figure 1. Absorption spectra of **I**, **II**, **III**, and **IV** in 1,2-dichloroethane (DCE). $[\text{Py}] = 1.7 \times 10^{-5} \text{ M}$; **I**, (—); **II**, (---); **III**, (····); **IV**, (-·-·-).

Although the qualitative absorption profiles are identical for **I** and **II**, the spectrum of **I** is broader than that of **II**. As a measure of broadness, the ratio of maximum absorbance at 346 nm (peak) to the minimum absorbance at 335 nm (valley) was calculated as shown in Table I.

Polymer effects on absorption spectra were found to depend on the solvent and degree of polymerization (*DP*). The spectral broadness of **II** was independent of solvent, but the difference in **I** and **II** could not be ascribed to interpolymer entanglement since the absorbance of both **I** and **II** satisfy Beer's law. The solvent dependent spectral broadening becomes more prominent with increasing *DP*.

Polymer chain conformation and consequently non-neighboring group participation may possibly be responsible for this.

Fluorescence Spectra

Examples of fluorescence spectra and their excitation profiles are shown in Figures 2, 3, and 4. Figure 2 shows that the broad exciplex emission between 450 nm and 500 nm (F_e) is much stronger for **I** than for **II**. As a measure of exciplex intensity, the ratio of F_e to F_m is taken, where F_m is the emission from the locally excited state of a pyrenyl group. As will be described in the following section, the F_e/F_m value of **I** varies with concentration whereas that of **II** does not. The F_e/F_m for **I** is always larger than that for **II**.

The excitation profile reflects the absorption spectra very well. Strictly speaking, exciplex is an excited state complex formed after excitation of a donor or an acceptor and excitation of a ground state complex should be excluded. As shown in Figure 3, the excitation profiles of polymer (**I**) depend on the monitoring wavelength. Since exciplex is formed *via* excitation of a DMA group, it is reasonable for there to be inconsistency in the exciplex-monitored and monomer-monitored excitation spectra in the short wavelength region. However, the spectra are also different in the S_0 — S_2 absorption region of pyrenyl group. Dependence of the excitation spectra on the monitoring wavelength is much smaller for **II**, as can be seen from Figure 4. These findings are presented in Table II, as valley/

Table I. Absorption spectroscopic data of I and II

Sample	Fraction No.	M_w	M_w/M_n	$\frac{DP}{n}$	$\epsilon \times 10^4$ ^1La	Hypochromicity %	Broadness of absorption spectrum ^c		
							<i>p</i> -Dioxane	Mesitylene	1,2-Dichloroethane
I	1	8500	1.22	17.2	1.47	57.4	0.52	0.56	0.40
	2	6200	1.15	12.6	1.83	47.2	0.42	0.44	0.40
	3	4600	1.18	9.3	2.20	36.2	0.40	0.42	0.39
	4	3400	1.25	6.9	2.47	28.4	0.39	0.42	0.39
	5	2600	1.20	5.4	2.60	24.6	0.39	0.42	0.39
II	10	1200	1.15	2.4	2.78	19.4	0.35	0.37	0.35
		589.7		1.0	3.45	standard	0.34	0.35	0.34

^a Relative to standard polystyrene.^b In *p*-dioxane.^c OD₃₃₅/OD₃₄₆ (valley/peak ratio). **Figure 2.** Fluorescence spectra of I, II, and III in mesitylene. [Py] = 2.0×10^{-5} M. Excitation at 344 nm. I, (—); II, (---); III, (-.-.-). **Figure 3.** Excitation spectra of I in DCE. Monitoring wavelength at 377 nm (—) and at 520 nm (-----). Maximum O.D., 0.04.

peak ratios of excitation spectra. The larger values correspond to broader spectra. Definitive comments on excitation profile should be made with caution since the spectral shape is a function of concentration. The results in Figures 3 and 4 are "true" emission corrected for exciting lamp and detector characteristics and obtained for extremely dilute solutions so that a linear correlation between concentration and emission intensity is maintained. Consequently, a good correspondence of the F_{337}/F_{346} value for emission monitored at 377 nm with the valley/peak ratio of absorption spectra in Table I in DCE is a meaningful result.

Concentration Dependence of Exciplex Emission

Both intrapolymer and interpolymer exciplex formations could be generally recognized. Con-

Figure 4. Excitation spectra of II in DCE. Monitoring wavelength at 377 nm (—) and at 520 nm (-----). Maximum O.D., 0.04.

centration dependence of F_e/F_m made possible the separation of these two types of exciplexes. The results measured in three solvents for the samples

Table II. The valley/peak ratio of excitation spectra of I (Fr-2) and II at different monitoring wavelengths^a

Monitoring wavelength	F_{337}/F_{346} ^b		F_{322}/F_{346} ^b	
nm	I	II	I	II
377	0.392	0.393	0.241	0.277
520	0.480	0.415	0.330	0.317
Difference %	+28.5	+5.6	+37.5	+14.4

^a Conditions: The maximum O.D. of sample solution was kept below 0.04. ([Py] < 10⁻⁶ M); solvent, 1,2-dichloroethane.

^b Suffixes indicate excitation wavelength in nm.

Figure 5. Concentration dependence of exciplex emission by I as a function of *DP* in *p*-dioxane. Excitation at 346 nm. I: Fraction 10 (●); 5 (◐); 4 (○); 3 (○); 2 (◐); 1 (○). II: (□). **Figure 6.** Concentration dependence of exciplex emission by I as a function of *DP* in mesitylene. Excitation at 346 nm. Symbols are the same as those in Figure 5. **Figure 7.** Concentration dependence of exciplex emission by I as a function of *DP* in DCE. Excitation at 346 nm. Symbols are the same as those in Figure 5.

fractionated by GPC are plotted in Figures 5, 6, and 7. The strongly concentration dependent exciplex formation by I indicates that the exciplex is formed mostly in an interpolymer manner whereas the contribution of intrapolymer exciplex as given by the F_e/F_m value at intrinsic dilution is almost identical to the concentration independent value for II. The non-linear F_e/F_m vs. concentration plots may in part be attributed to the overlap of the exciplex emission with the monomer emission. As shown in Figure 2, there seems to be a certain amount of contribution of F_e toward F_m but not *vice versa* and hence the apparent F_m value tends to be larger than the actual value. This tendency increases with increasing F_e/F_m and consequently, F_e/F_m vs. C plots convex upwards with increasing C . This effect would be more pronounced in nonpolar solvents in which F_e is blue-shifted and mixing of F_e to F_m increases. If this were the reason for the non-linear plots in Figures 5, 6, and 7, the shapes of plots in a solvent should be identical regardless of *DP*. The shape of F_e/F_m vs. C plots is related to fundamental problems of polymer solution and cannot be treated as a trivial technical problem.

As reference experiments the well-known pyrene-*N,N*-dimethylaniline exciplex was examined under the same instrumental conditions to Figures 5, 6, and 7. Deviation from linear relation begins at $F_e/F_m \approx 3$ in mesitylene. In *p*-dioxane or 1,2-dichloroethane, exciplex emission intensity is low and the deviation from linearity was not detected (Figure 8). Nonlinear relation between F_e/F_m and C in the

Figure 8. Concentration dependence of exciplex emission between **III** and **IV** in mesitylene (●), *p*-dioxane (○), and DCE (○). $[Py] = 4.0 \times 10^{-5}$ M. Excitation at 344 nm.

Figure 9. Wavelength of maximum exciplex emission as a function of concentration. **I** in mesitylene (●), **I** in DCE (○), **II** in mesitylene (■), **II** in DCE (□).

polymeric system starts from the beginning at very low F_e/F_m value.

Concentration effects could also be observed on the exciplex emission wavelength. The red shift of the exciplex emission peak of **I** in DCE amounts to 20 nm with increasing concentration, but no such effect could be observed in mesitylene, as evident from Figure 9. Furthermore, the peaking wavelength of intramolecular exciplex by **II** was independent of concentration. These phenomena seem to possibly result from the different environments in which intra- and interpolymer exciplex formations take place.

DISCUSSION

Ground State Interaction between Chromophores Shown by Absorption and Excitation Spectra

The ground state interactions of exciplex forming systems were studied for pyrene-DMA,⁹ anthracene-DMA, DMA or *N,N*-diethylaniline-1,2,4,5-tetracyanobenzene and 1-(2- or 9-anthryl)-3-(*p*-*N,N*-dimethylaminophenyl)propane.¹⁰ As far as the pyrene-DMA system is concerned, there is obviously weak molecular association at room temperature. In the low temperature matrix, ground state interactions between chromophores capable of forming exciplex in the excited state become more pronounced. Recently, we found EDA (electron donor acceptor) fluorescence by the present polymer in 2-methyltetrahydrofuran matrix at 89 K.¹¹ A detailed discussion on the EDA emission will be published in the near future. The results seem comparable to the spectroscopic characteristics of a concentrated pyrene-DMA system in a low temperature matrix. Such weak but definite ground state interactions probably influence the absorption spectra of the polymer.

As shown in Figure 1 and Table I, the absorption spectra of the pyrenyl groups broader in polymer than in the dimer model compound, and consequently the smaller apparent value of $\epsilon_{\max}$ indicate weak ground state interaction in the polymer system. Furthermore, as shown in Figure 10, the absorption spectra becomes broader when the molecular weight of the polymer increases and a poor solvent is used. The apparent values of $\epsilon_{\max}$ are independent of the polymer concentration below 2×10^{-5} mol dm⁻³, indicating that the ground state interaction is almost intramolecular. The excitation spectra of exciplex fluorescence of the polymer monitored at 520 nm is broader than that monitored at 377 nm, and the excitation spectra of **I** is broader than that of **II** as shown in Table II. It seems that the pyrene-DMA interaction in the ground state participates in the exciplex formation at the excited state as follows;

Figure 10. Broadness of absorption spectra of **I** as a function of DP . Solvent: mesitylene (●); *p*-dioxane (◐); DCE (○).

Figure 11. Effects of excitation wavelength on the shape of exciplex emission. Sample: **I** (fraction 2) in DCE. Excitation at 344 nm (—) and 365 nm (-----).

Participation of a weak EDA interaction is shown by the excitation wavelength dependence of the exciplex-like emission. Figure 11 demonstrates a shift of the peaking wavelength of **I** when the **I** solution is excited at the long wavelength edge of absorption. If one admits the broadening of absorption spectra as due to EDA interaction, the photoabsorbing species responsible for exciplex-2 is concluded to be the ground state complex.

To the best of our knowledge, the phenomenon of the excitation wavelength dependent exciplex emission has not been reported so far. In accordance with a strict definition of an exciplex, exciplex-2 may not actually be called an exciplex. Fluorescence by such bulky large molecules in the condensed

phase should be emitted from the lowest excited energy level identical for both exciplexes 1 and 2. As suggested by the wavelength of emission from exciplex-2, which is shorter than that from exciplex-1, direct excitation of EDA complex might bring about emission from non-relaxed states. If so, the rise in fluorescence in the time region from ps to sub-ns as a function of exciting wavelength would provide key information. This is beyond the scope of present paper and should be treated as a problem in pure photophysics.

In contrast to the wavelength shift in Figure 11, the interpolymer association of **I** in DCE causes the red shifts of exciplex emission. Although this polymer association is interpreted as due to pyrene-DMA interaction, its nature is very different from the intrapolymer EDA interaction as evidenced by the concentration independent broadening of the absorption spectra. If the emission wavelength shift in Figure 9 were due to the contribution of exciplex 2, the direction of the shift would be opposite. The results in Figure 9 indicate the change in exciplex forming environments for a single species while Figure 11 suggest the presence of two exciplex-like species. It should be noted that the interpolymer exciplex disappears in MTHF glass matrix.¹¹ Polymer association provides favorable exciplex forming environments but not the equivalent of a preformed excimer site.

In comparison with the excimer forming analogues polyesters, spectral differences are distinctive. Polyesters containing pyrenyl groups alone show much sharper absorption and excitation spectra than **I**. Furthermore, association of the pyrenyl groups could not be detected.^{12,13} Recently we synthesized a reference polyester of **I** having an identical skeletal structure with **I** but having a phenyl group instead of a DMA group.¹⁴ The polyester exhibits only intrapolymer excimer supporting our conclusion that the spectroscopic characteristics of **I** stem from weak EDA pairing.

Solvent Effects on Intensity and Wavelength of Exciplex Emission

The general effects of increasing solvent polarity upon intermolecular exciplex formed between small molecules are a shift of the peaking wavelength to a longer wavelength region and a decrease in the intensity and lifetime of the exciplex emission. Being a diffusion controlled process, an increase in solvent

viscosity also results in a reduced exciplex forming probability. The relative exciplex emission intensity (F_e/F_m) in small molecular systems is shown as a function of the concentration of **IV** in Figure 8. The F_e/F_m value is higher in non-polar mesitylene ($\epsilon = 2.28$, $\eta = 0.94$) than in 1,2-dichloroethane ($\epsilon = 10.36$, $\eta = 0.73$) as expected. In a polymer system, an additional factor of the polymer chain solubility which determines the polymer chain dimensions in a solution should be considered. To study this particular solvent effect, two solvents having comparable polarity and viscosity but different polymer solubility were chosen. Mesitylene and *p*-dioxane are nearly identical from the stand point of polarity and viscosity whereas the intrinsic viscosity of **I** ($[\eta]$) is 0.035 and 0.07 in mesitylene and *p*-dioxane, respectively. Apparently *p*-dioxane is a better solvent. Although the general trend of the plots in Figures 5 and 6 are similar, the F_e/F_m value decreases more rapidly in mesitylene with increasing *DP*. In a concentration region above 1×10^{-5} M, the exciplex is nearly interpolymer. The difference between Figures 5 and 6 suggests that a shrunk polymer chain in poor solvents is unsuitable for interpolymer association. The trend of interpolymer association is more pronounced in DCE which is the best solvent of all.

The following information was derived from Figures 5, 6, and 7. i) F_e/F_m increases with concentration for the medium *DP* samples, indicating interpolymer association. ii) In contrast to **I**, **II** shows concentration independent exciplex emission. iii) There is very little *DP* effect on the intramolecular exciplex formation since the F_e/F_m values at infinite dilution converge to a single value identical to that of **II**. iv) In comparison with the combination of **III** with **IV** shown in Figure 8, the F_e/F_m values of **I** and **II** are extremely large. To obtain equivalent values of F_e/F_m in the monomer model system, the concentration of DMA must be of the order $10^{-1} \sim 10^{-2}$ mol dm⁻³. Consequently, the local concentration of DMA in the polymer system is assumed to be 10^4 times higher than the nominal concentration. Molecular weight and solvent dependent saturation phenomena of F_e/F_m are of the most interest. As already discussed the phenomenon is more pronounced in a poor solvent than in a good one.

The self-association of **I** occurs allosterically only in good solvents.⁸ A detailed measurement of F_e/F_m

in the concentration region as low as 10^{-7} mol dm⁻³, shows that the F_e/F_m vs. *C* plots concave upward in DCE but not in mesitylene. For an efficient intermolecular interaction to take place, the polymer chain must be extended. When the polymer chain shrinks in a poor solvent, the number of intermolecular interaction sites becomes small. Furthermore, the polymer continues to shrink more and more as intermolecular interaction proceeds, implying the saturation of F_e/F_m vs. *C* plots in a poor solvent. The constancy of the exciplex wavelength vs. *C* plots in Figure 9 seems to be consistent with the poor solvation of **I** in mesitylene. In the case of a shrunk polymer chain, interpolymer association does not affect the chain conformation and thus neither the environment of the exciplex formation very much.

Generally speaking, solvent effects in a polymeric system are not as pronounced as in a monomer model system.^{1,7} The polymer main chain often plays the role of solvent and the extent of solvation in a polymeric system is less than that in a small molecular system. It is immediately apparent on comparison of Figure 8 with Figures 5–7 that the solvent effects on F_e/F_m in Figure 8 cannot explain the results shown in Figures 5–7. Neither the intrapolymer exciplex $[(F_e/F_m)_{c \rightarrow 0}]$ nor the interpolymer exciplex $[(F_e/F_m)_{c \rightarrow \infty}]$ in the three solvents follow the sequence, mesitylene > *p*-dioxane > DCE, as demonstrated in Figure 8. Chain conformation is thus concluded to be a predominant factor in determining the behavior of a polymer exciplex.

Molecular Weight Effect on Exciplex Formation

Polymer chain conformation in a solvent is also a function of *DP*. Although intrapolymer exciplex intensity is independent of *DP*, interpolymer association is strongly *DP* dependent. As a measure of interpolymer association, the initial slopes of the F_e/F_m vs. *C* plots are plotted against *DP* in Figure 12. There is an optimum *DP* promoting the interpolymer exciplex formation. Furthermore, the optimum *DP* shifts toward a higher value with increasing polymer-solvent affinity. If the polymer chain is well extended, interpolymer association is facilitated with increasing *DP*, since the zipping effect participates more efficiently. When *DP* increases beyond the maximum value, the polymer chain begins to contract and therefore the available

Figure 12. *DP* Dependence of interpolymer interaction of I in mesitylene (●), *p*-dioxane (●), and DCE (○).

contact area for interpolymer exciplex formation falls off, reducing the tendency of interpolymer exciplex formation.

There is a broad correlation between the data in Figure 11 and the spectral broadening as a function of *DP* shown in Table I and plotted in Figure 12. The spectral broadening is exclusively an intrapolymer phenomenon and expected to increase with shrinkage of the polymer chain. In DCE, the valley/peak ratio in Figure 11 is fairly constant whereas in mesitylene and *p*-dioxane, the values increase very much in the *DP* region where interpolymer exciplex formation becomes inefficient.

CONCLUSION

Interpolymer association in dilute solutions was unequivocally demonstrated and the determining factors have been qualitatively discussed. This research provides a clearer view on "polymer effects". Although local concentration effect is an important aspect of polymer effects, the present study indicates that a high local chromophore concentration may possibly be a negative factor for interpolymer association. For polymer self association, a well-defined, regular primary structure is an essential requirement. Such a polymer is in a "structure-matched state" for self-association. When electron donating

and electron accepting vinyl compounds were subjected to random copolymerization, the exciplex emission was purely intrapolymer.¹⁵ Also, we have demonstrated the structure-matching effect in complex formation of carbazole polymers with acceptor polymers.¹⁶

The present results are encouraging since they indicate that extensive interpolymer association can be brought about by integration of very weak intermolecular forces provided the chemical structure and chain conformation are optimized. Research is now being carried out to examine a series of exciplex forming polymers with different chromophore intervals and different main chain structures.

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